

## Sources and Composition of PM<sub>2.5</sub> at the National Energy Technology Laboratory in Pittsburgh during July and August 2000

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PM<sub>2.5</sub> mass was measured daily with three batch samplers, a PM<sub>2.5</sub> R&P Partisol-Plus FRM, an Andersen RAAS, and a BYU PC-BOSS, and continuously with a TEOM monitor during July and August 2000. PM<sub>2.5</sub> composition was also determined. These data are part of an ongoing PM<sub>2.5</sub> characterization program centered around a sampling site at the National Energy Technology Laboratory Pittsburgh campus. The composition and concentrations of PM<sub>2.5</sub> were both highly variable during this time period. Likely sources of PM<sub>2.5</sub> during low concentration periods were transportation, coal-fired boiler, and other emissions generated in the local area. For these periods, the average concentration of PM<sub>2.5</sub> was 13  $\mu\text{g}/\text{m}^3$  and 70% of the PM<sub>2.5</sub> mass was carbonaceous material, including semivolatile organic material that was lost in varying degrees from both the TEOM and FRM samplers. In contrast, much higher concentrations of PM<sub>2.5</sub> were associated with transport of pollutants to the site. Analysis of meteorological and back-trajectory data suggests that these pollutants were emitted elsewhere during a period of high atmospheric pressure and were subsequently transported to the site with the passage of a frontal system. When the PM<sub>2.5</sub> collected at the site originated from the west or southwest, the concentrations averaged 31  $\mu\text{g}/\text{m}^3$  and ammonium sulfate averaged 54% of the PM<sub>2.5</sub> mass. Scanning electron microscopy and trace element analyses are consistent with the association of high concentration PM<sub>2.5</sub> episodes with transport of coke and iron processing, coal-fired boiler, and other emissions from the Ohio River Valley region to the NETL site. Preliminary observations on the use of SEM and PIXE data in source apportionment at the NETL site are given.

### Introduction

Airborne particulate matter has been shown to have adverse effects on human health and the environment. On July 17, 1997, the U.S. Environmental Protection Agency<sup>1</sup> revised the National Ambient Air Quality Standards (NAAQS) to address ambient air concentrations of particulate matter with an aerodynamic diameter of 2.5 micrometers or less (PM<sub>2.5</sub>). The new PM<sub>2.5</sub> standard<sup>2</sup> establishes a 24-h average concentration limit of 65  $\mu\text{g}/\text{m}^3$  and an annual mean concentration limit of 15  $\mu\text{g}/\text{m}^3$  to protect human health from possible chronic and acute effects associated with the inhalation of fine particles. In response to the National Research Council's recommendation to improve the characterization of the

potential health-related components of PM<sub>2.5</sub>,<sup>3</sup> the National Energy Technology Laboratory (NETL) Office of Science and Technology (OST) has established, equipped, and operated a PM<sub>2.5</sub> sampling and analysis site at the Pittsburgh NETL campus. Details of this program have been published separately.<sup>4</sup> There are two main driving force behind this monitoring effort. One is the association that exists between the mass concentration of PM<sub>2.5</sub> and morbidity and mortality among human subjects.<sup>5–7</sup> The second is the need for a better understanding of

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(1) U.S. Environmental Protection Agency. Revised Requirements for Designation of Reference and Equivalent Methods for PM<sub>2.5</sub> and Ambient Air Quality Surveillance for Particulate Matter: Final rule. U.S. Environmental Protection Agency, 40 Code of Federal Regulations Parts 53 and 58; In *Federal Register* (62FR 38763); U.S. Government Printing Office: Washington, DC, July 18, 1997.

(2) Musick, D. A Summary of the Ambient Air Program for PM<sub>2.5</sub>. *Environ. Manager* 1999, February 17–20.

(3) U.S. Nuclear Regulatory Commission. Research Priorities for Airborne Particulate Matter, Immediate Priorities and a Long-range Research Portfolio. NRC Report; National Academy Press: Washington, DC, 1998.

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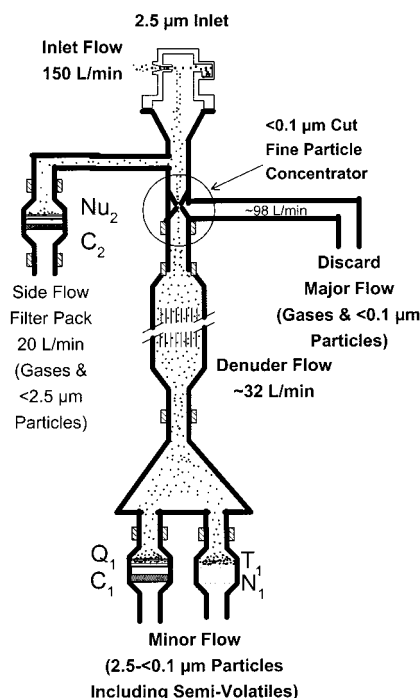
the relationships among concentrations and composition of ambient  $\text{PM}_{2.5}$  and the sources and atmospheric processes that contribute to those concentrations.<sup>3</sup>

Sampling at the NETL  $\text{PM}_{2.5}$  site was initiated at the NETL Pittsburgh campus, located in a suburban area 20 km southwest of the Pittsburgh city center, in October 1999. A companion paper<sup>4</sup> has outlined the sampling program and given results for  $\text{PM}_{2.5}$  mass,  $\text{PM}_{2.5}$  carbonaceous components, and precursor gases ( $\text{SO}_2$ ,  $\text{NO}_x$ ,  $\text{NO}_2$ ,  $\text{O}_3$ , and  $\text{CO}$ ) during the initial year of the effort. Relationships among various measured parameters and possible causes of the variations seen in concentrations of the species monitored were explored. Correlation of the data with meteorological data and back-trajectory analyses suggested that episodes of high concentrations of  $\text{PM}_{2.5}$  are associated with transport of pollutants from outside the NETL study site area during the passage of frontal systems. Pollutants that build up in other areas during high-pressure regimes are transported to the site under these conditions. The main sources of these transported pollutants were from the general direction of the Ohio River Valley to the west and southwest of the site. The transport of this  $\text{PM}_{2.5}$  occurred most frequently and resulted in the highest concentrations during the summer. Local sources, within a 20 Km radius of the NETL site, were minor contributors to elevated  $\text{PM}_{2.5}$  concentrations. This paper explores the chemical composition of the  $\text{PM}_{2.5}$  at the NETL site during the period from mid-July through August, 2000. Changes in the composition associated with transport of pollutants to the site are discussed, and the probable sources of  $\text{PM}_{2.5}$  at the site as a function of meteorological conditions are considered.

### Experimental Section

**The NETL Sampling Site.** The air monitoring site is located on an open hill at the NETL Pittsburgh campus. Since the NETL site is not near any major road or freeway, high concentrations of fresh automotive emissions are not expected. No major point sources of air pollutants are close to the site. Two experimental combustors, a 500 lb/h pulverized coal-fired combustion research facility and a 40 lb/h combustion environmental research facility (CERF), which burns a variety of fuels, are occasionally operated at the NETL facility just 200 m east of the sampling site. About 600 m east by southeast is a coal-fired steam plant that burns up to 1900 lb/h to provide heating for the NETL facility. Each of these sources are downwind of the NETL site the great majority of the time. While they make infrequent contributions to concentrations of nitrogen and sulfur oxides and  $\text{CO}$ , they are not a significant contributor to  $\text{PM}_{2.5}$  at the site.<sup>4</sup> Two coal-fired power plants (410 and 450 MW) are located about 10 km to the southeast. Major coal-fired power plants and chemical manufacturing plants are located along the Ohio River to the west and southwest of the NETL site. Iron and coke processing facilities and steel finishing mills are located along the Monongahela River to the east of the facility and the upper Ohio River valley to the west and northwest. These are all potential sources of transported pollutants to the site. Since the prevailing winds at the site are from the southwest to northwest directions, impacts from emissions from the Ohio River Valley and urban centers to the west are expected.<sup>4</sup>

**Sample Collection.** The air monitoring station<sup>4</sup> consists of an indoor facility housing equipment to continuously monitor gaseous pollutants ( $\text{SO}_2$ ,  $\text{NO}_x$ , and  $\text{NO}_2$  data are used in this paper) and  $\text{PM}_{2.5}$  particulate carbon. A fully instrumented, 14-bay outside rack also supports a variety of  $\text{PM}_{2.5}$  samplers.



**Figure 1.** Schematic of the PC-BOSS.

Equipment from which data used here were taken include: a  $\text{PM}_{2.5}$  Partisol-Plus model 2025 FRM Sequential Air Sampler (Ruppel & Patashnick (R&P), Albany, NY) for the 24-h determination of  $\text{PM}_{2.5}$  mass, a  $\text{PM}_{2.5}$  model 1400ab TEOM (tapered element oscillating microbalance) ambient particulate monitor (R&P) for the continuous measurement of  $\text{PM}_{2.5}$  mass, a  $\text{PM}_{2.5}$  model 5400 ambient carbon particulate monitor (R&P) for the continuous measurement of  $\text{PM}_{2.5}$  carbon, a  $\text{PM}_{2.5}$  RAAS 2.5–400 Speciation Sampler (Thermo Andersen, Smyrna, GA) for the periodic determination of fine-particulate composition, and monitors for the continuous measurement of  $\text{SO}_2(\text{g})$  (Advanced Pollution Instrumentation (API), San Diego, CA, model 100A chemiluminescent monitor), and  $\text{NO}_x$  and  $\text{NO}_2$  (API model 200A Fluorescent Monitor). The various gas analyzers were calibrated weekly using a Dynamic Dilution Calibrator (API model 700) and certified gas standards. The mass collected on all 24-h integrated filter samples collected with the various  $\text{PM}_{2.5}$  integrated samplers was determined at the Pittsburgh Technology Center Mine Safety and Health Administration laboratory using the FRM  $\text{PM}_{2.5}$  protocols.<sup>8</sup> In addition to the NETL samplers, Brigham Young University also provided a PC-BOSS<sup>9</sup> sampler for the 24-h determination of fine-particulate composition, including the semivolatile nitrate and organic material. The operation of the PC-BOSS at the site has been described.<sup>10</sup>

The samples for the determination of  $\text{PM}_{2.5}$  chemical composition were all collected from noon Eastern daylight time on each sampling day to noon the next day. PC-BOSS samples were collected every day during the 15 July to 31 August time period considered in this paper. A schematic of the PC-BOSS sampler is given in Figure 1. Fine-particulate elemental content was determined from samples collected on a polycar-

(8) U.S. Environmental Protection Agency. Quality Assurance Guidance Document Method Compendium:  $\text{PM}_{2.5}$  Mass Weighing Laboratory Standard Operating Procedures for the Performance Evaluation Program. U.S. Environmental Protection Agency Office of Quality Planning and Standards: Research Triangle Park, NC 27711, 1998.

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bonate filter (47-mm, 0.4- $\mu$ m pore, Gelman Sciences, Ann Arbor, MI, Nu<sub>2</sub> in Figure 1) taken from a side-flow stream sampled before the PC-BOSS particle concentrator and denuder<sup>10,11</sup> and on a Teflon filter (47-mm, Teflur, Whatman) in the PM<sub>2.5</sub> FRM sampler. Concentrations of chemical constituents were determined from particles collected after a particle concentrator and BOSS charcoal denuder<sup>9,10</sup> (Figure 1) to remove gas-phase SO<sub>2</sub>, HNO<sub>3</sub>, and semivolatile organic compounds (SVOC) with an efficiency which exceeds 99%. The denuder was followed by two parallel filter packs. One filter pack contained a 47-mm quartz filter (Gelman, Q<sub>1</sub> in Figure 1) followed by a 47-mm charcoal impregnated glass fiber filter (CIG, Schleicher and Schuell, Dassel, Germany, C<sub>1</sub> in Figure 1). This combination of filters was used to determine fine-particulate carbonaceous material, sulfate, and nonvolatile nitrate on the quartz filter, and semivolatile nitrate and organic material lost from the particles on the quartz and trapped on the sorbent CIG. The other filter pack contained a 47-mm Teflon filter (Whatman Teflur, T<sub>1</sub> in Figure 1) followed by a Nylasorb filter (Gelman Nylasorb, N<sub>1</sub> in Figure 1). The Teflon filter was used to determine mass, sulfate, and nonvolatile nitrate. The Nylasorb filter was used for the determination of nitrate lost from particles during sampling. With this combination of techniques, negative sampling artifacts are avoided.

Concentrations of PM<sub>2.5</sub> mass were determined daily from the Teflon filters of the PM<sub>2.5</sub> Partisol-Plus FRM sequential air sampler. These filters were also used to determine either fine-particulate sulfate or trace metals. The composition of PM<sub>2.5</sub> was determined every other day from August 6–19 using the PM<sub>2.5</sub> RAAS 2.5–400 speciation sampler. The configuration of the RAAS during collection of these samples included a Pd-coated 47-mm polycarbonate filter after a short BOSS denuder<sup>11</sup> for scanning electron microscopy analysis of collected particles<sup>12</sup> sampled at 7.3 L/min, and a filter pack with 47-mm quartz and CIG filters sampled at 16.7 L/min downstream of a short BOSS denuder.<sup>13</sup> The denuders in the RAAS were used to avoid possible artifact collection of reactive gases by the subsequent filters.

All quartz filters were baked at 800 °C for 24 h before use. The CIG sorbent filters were pretreated by baking in N<sub>2</sub> at 330 °C for 24 h prior to use. The Teflon, polycarbonate, and Nylasorb filters were used as received from the manufacturer. Field-handled blank samples were obtained for about 10% of all samples.

**Sample Analysis.** *Analysis for Nitrate and Sulfate.* Sulfate and nitrate analysis was by ion chromatography. All ion chromatographic analyses for PC-BOSS samples were performed using a Dionex LC20 chromatograph equipped with a CD20 conductivity detector. The eluent was 3.5 mM Na<sub>2</sub>CO<sub>3</sub>/1.0 mM NaHCO<sub>3</sub> solution at a flow rate of 1.2 mL/min, and the suppressor was an anion self-regenerating suppressor. A similar approach was used at NETL for analysis of the PM<sub>2.5</sub> FRM Teflon filters. One 2-cm<sup>2</sup> punch of the quartz filters was extracted by ultrasonication with 5-mL of deionized water in a Monovette (Sarstedt, Newton, NC). The extracted solution was analyzed for sulfate and nitrate. Whole Teflon filters (from either the PC-BOSS or PM<sub>2.5</sub> FRM samplers) and half of the PC-BOSS polycarbonate filters were also extracted by ultrasonication in deionized water and analyzed for sulfate and nitrate. One 2-cm<sup>2</sup> punch from each CIG filter was extracted

by ultrasonication in a 1% acetone–eluent solution<sup>14</sup> and analyzed for nitrate. Whole Nylasorb filters were extracted ultrasonically in eluent solution and analyzed for nitrate.

Although the NETL analysis of the PM<sub>2.5</sub> FRM Teflon filters also included a separate ion-chromatographic analysis for ammonium cations, for simplicity and to facilitate the direct comparison of fine-particulate mass concentration from a variety of types of filters, ion-chromatographic sulfate and nitrate ion concentrations were converted to the corresponding theoretical ammonium sulfate and ammonium nitrate weight concentrations. Preliminary analysis of the FRM Teflon filter data indicates that for six of the twenty-four samples for which ammonium, nitrate, and sulfate ion concentrations were available, a significant molar portion of the ammonium sulfate, 25–80%, was present as ammonium hydrogen sulfate. However, on a weight basis, this amounts to only a 3–10% overestimation of the ammonium sulfate weight concentration.

*Analysis for Collected Carbonaceous Material.* A 2-cm<sup>2</sup> portion of the quartz and CIG filters were analyzed for carbonaceous material by thermal desorption of the collected materials using temperature programmed volatilization.<sup>14,15</sup> The carbonaceous materials were converted to CO<sub>2</sub> which was then measured using a nondispersive infrared (NDIR) detector on an ULTRAMAT 3 gas analyzer (Siemens Inc., Roswell, GA). The NDIR detector was calibrated using three certified CO<sub>2</sub> standards that spanned the analysis concentration range. Organic compounds evolved from the particles and collected by the CIG filter were considered as semivolatile (SVOC). The CIG filters were heated from 50 °C to about 350 °C at a ramp rate of 10°/min in a stream of nitrogen. The maximum temperature used during volatilization of the SVOC collected on the CIG filters was imposed by the fact that degradation of the filter charcoal began 10–20 °C below the maximum analysis temperature. The quartz filters were heated from 50 °C to 800 °C at a ramp rate of 28°/min in a stream of N<sub>2</sub>/O<sub>2</sub> (70:30% v/v). Soot, if any, was estimated from the high temperature (usually above 400 °C) peak<sup>14</sup> on the thermogram obtained from the quartz filter analysis. Because of the presence of high concentrations of secondary organic material which evolved at a temperature just below that for soot, the precision of this estimate is about 30–50%. The thermograms indicated that all collected organic compounds and soot were evolved from the collection matrix at the maximum temperatures used. No evidence for the high-temperature evolution of CO<sub>2</sub> from inorganic carbonates was seen. Blank determinations were made for both quartz and CIG filters.

*SEM Analysis.* The RAAS sampler, palladium coated, polycarbonate filters were prepared for computer controlled scanning electron microscopy (CCSEM) analysis<sup>12</sup> by cutting wedges from the filters and mounting them on a substrate with double sided adhesive silver tape. Images and EDX elemental spectra were collected on approximately 1200 particles per sample using The Personal SEM (Aspex Instruments). The SEM was run in the secondary electron imaging mode for maximum resolution of particles down to 0.16- $\mu$ m diameter. Two magnifications were used: 1000 $\times$  and either 500 $\times$  or 200 $\times$ .

Instrument parameters included 15 kV accelerating voltage, sample working distance of 16 mm, 7-s EDX spectra acquisition for each particle, and multiple beam current checks with an internal Faraday cup during each filter analysis. Grey level threshold checks were periodically made to compensate for small variations in image brightness and contrast due to sample charging effects. Magnification and X-ray calibrations were

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also incorporated into each analysis. EDX spectra, collected at 15 kV on traceable reference standards, were used in developing a spectral library for reference during the analyses.

The EDX carbon-to-palladium ratio was used to differentiate carbonaceous particles from the residual carbon background signal emanating from the polycarbonate filter. The C:Pd ratio threshold value had to be determined on an individual filter basis by collecting multiple background particle free spectra on each individual filter sample, because the palladium coating thickness varied from 0.15 to 0.25- $\mu\text{m}$  thickness.

This combination of SEM parameters provided a reproducible baseline and standard for particle speciation and comparative analysis of the observed particles. At the completion of the CCSEM analysis, the individual particle data were entered into a database and sorted into classification bins based on particle chemistry, size and morphology. The particle concentrations in each bin were expressed on a volume percent basis and converted to a mass/ambient air volume basis using the gravimetrically determined  $\text{PM}_{2.5}$  mass concentration for that sample. Three bins of particular interest for this paper were spherical aluminosilicate (SAS) particles, iron rich spherical particles and calcium/sulfur rich particles. The SAS particles are characteristic of emissions from coal-fired power plants and comprise essentially all the primary emissions from these facilities.<sup>12</sup> Small, less than 2.5  $\mu\text{m}$ , calcium oxide and Fe rich spherical particles are expected to be emitted from iron processing industries. The Ca/S particles may be formed in transit from calcium oxide particles reacting with atmospheric  $\text{SO}_2$  and  $\text{O}_3$ . Calcium oxide particles may originate from other sources including lime processing facilities, cement processing facilities, fugitive dust from construction/demolition of concrete structures, but particles emitted from such sources are generally greater than 2.5  $\mu\text{m}$  in size and few of these sources exist in the region.

**PIXE Analysis.** Elemental concentrations in the particles collected on selected Teflon filters of the  $\text{PM}_{2.5}$  FRM sampler or polycarbonate filters of the PC-BOSS were determined using proton induced X-ray emission analysis, PIXE.<sup>16</sup> A small, clear-plastic frame with a 0.95-cm diameter hole in the middle was sprayed with mastic on one side. A 1.44-cm<sup>2</sup> (1.2 cm  $\times$  1.2 cm) square portion of the 47-mm sample filter, taken near the edge of the filter, was cut with the aid of a template. This portion of the sample could then be placed in the analysis chamber. The PIXE analysis used a 2.1-MeV proton beam from an AN2000 (High Voltage Engineering) Van de Graaff accelerator. The proton beam passed through a 1.1-mg/cm<sup>2</sup> pyrolytic graphite foil (Pfizer, Minerals Pigments & Metals Division) and the diffused beam was collimated with graphite apertures to provide a uniform beam spot of 0.29 cm<sup>2</sup> on the air filter sample. The sample surface was positioned at an angle of 56° to the proton beam axis and the X-ray detector axis was at 90° to the beam axis. Protons passing through a sample were collected in a Faraday cup and the proton charge collected was measured. Filter samples were irradiated with a 15-nA proton beam until 40  $\mu\text{C}$  of charge was collected. An X-ray filter was placed between the sample and detector system. The filter had a 46.0- $\mu\text{m}$  (8.52 mg/cm<sup>2</sup>) thick beryllium foil and a 356- $\mu\text{m}$  (48.4 mg/cm<sup>2</sup>) thick Mylar foil. The Mylar foil had a hole in the center of 0.27-mm diameter. The area of the hole was 0.89% that of the 30-mm<sup>2</sup> detector area. This filter allowed the intense, low-energy X-rays from light elements to pass primarily through the hole and on to the detector while less intense, but more energetic X-rays from elements heavier than potassium would pass through the Mylar as well. The X-rays were detected using an energy-dispersive X-ray spectrometer (Noran Instruments, Inc., model TX-3/48-10206). The Si(Li)

detector had a surface area of 30 mm<sup>2</sup> and thickness of 3 mm with an energy resolution at the Mn K $\alpha$  line of 170 eV under analysis conditions. Electronic pulses from the spectrometer were processed by a Noran TX-513A amplifier, digitized by a Canberra 8075 analogue to digital converter (ADC), and the X-ray spectrum was stored in a Canberra Series 90 multi-channel analyzer (MCA). Digital X-ray spectra were analyzed by the computer program GUPIX (Department of Physics, University of Guelph, Guelph, Ontario, Canada). The final element concentrations were calculated, organized, and presented in the spread-sheet program EXCEL (Microsoft). The element concentration calibration was achieved by the use of X-ray thin film standards acquired from MicroMatter Co. These contain about 50  $\mu\text{g}/\text{cm}^2$  (with an uncertainty of 5%) of pure element or compound deposited on a thin film of Mylar or Nuclepore filter. More than 30 elements were used. The response of a MicroMatter Mn film standard is determined and then the same standard was analyzed one or more times each day to check the system for X-ray energy calibration, detector resolution, and correct quantitation. The response of the Mn standard varies from day to day by zero to a few percent. This variation was used to compute a daily factor and the calibration is corrected by this factor. The calibration of the PIXE system was regularly checked using NIST Standard Reference Material 1832, Thin glass Film on Polycarbonate. This SRM has the following elements: Na, Al, Si, Ar, Ca, V, Mn, Co, and Cu.

## Results and Discussion

**Data Comparisons.** There are several measures of  $\text{PM}_{2.5}$  mass and composition which can be intercompared.

**Fine-Particulate Sulfate.** Fine-particulate sulfate was determined on both the quartz ( $Q_1$  in Figure 1) and Teflon ( $T_1$  in Figure 1) minor flow filters of the PC-BOSS and on some of the Teflon filters of the FRM sampler. As indicated in Table 1, the various results agree. The agreement between the PC-BOSS Teflon and quartz filters of the PC-BOSS ( $\sigma = \pm 0.75 \mu\text{g}/\text{m}^3$ ,  $\pm 7.7\%$ ) is an estimate of the precision of the PC-BOSS data. The agreement between the Teflon and quartz filter average PC-BOSS ammonium sulfate and the FRM Teflon filter ammonium sulfate ( $\sigma = \pm 0.80 \mu\text{g}/\text{m}^3$ ,  $\pm 7.8\%$ ) is an estimate of the precision of the correction of the PC-BOSS data for the particle concentrator efficiency.<sup>9,10</sup> The precision estimates for these two independent evaluations of the data are comparable. The concentrations of ammonium sulfate determined from the minor flow data of the PC-BOSS ( $Q_1$  and  $T_1$  in Figure 1) and those calculated from the PIXE data for the polycarbonate side-flow filter of the PC-BOSS are also compared in Table 1. The expected precision of the PIXE data is  $\pm 15\%$ . The IC and PIXE data agree within this expected precision.

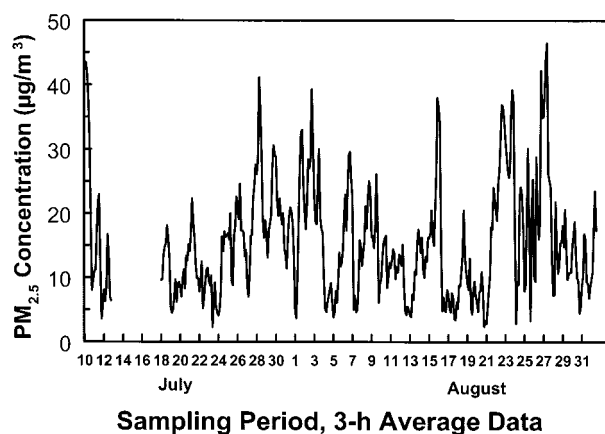
**Fine-Particulate Mass and Organic Material.** Fine-particulate mass was calculated on a 3-h average basis from the 1/2-h average TEOM monitor data. In addition, the 24-h average  $\text{PM}_{2.5}$  mass was measured with the FRM sampler and also constructed from the various analyzed components of the PC-BOSS.  $\text{PM}_{2.5}$  is composed of a wide range of species, but in this article particulate composition is assumed to be carbonaceous material consisting of both elemental (soot) and organic (assumed to be 61% carbon<sup>17</sup>) carbon, sulfate as ammonium sulfate, nitrate as ammonium nitrate, and crustal material. The constructed mass of nonvolatile components was calculated from the PC-BOSS data as

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**Table 1. Results of the Statistical Comparison of Sulfate and Mass Measurements,  $\mu\text{g}/\text{m}^3$** 

comparison (X vs Y)	N	$R^2$	slope <sup>a</sup>	intercept <sup>a</sup>	$Se_y^a$	X	bias	$\sigma^b$	% $\sigma$
<b>ammonium sulfate</b>									
PC-BOSS	45	0.96	$1.04 \pm 0.03$	0	1.2	9.5	-0.3	0.75	7.7
teflon vs quartz		0.97	$0.98 \pm 0.03$	$0.5 \pm 0.3$	1.1				
PC-BOSS vs FRM	17	0.96	$1.04 \pm 0.05$	0	1.4	10.0	-0.6	0.80	7.8
		0.96	$1.09 \pm 0.05$	$-0.5 \pm 0.6$	1.4				
PC-BOSS vs PIXE	14	0.82	$1.04 \pm 0.06$	0	3.3	11.5	-1.0	2.05	17
		0.84	$0.93 \pm 0.12$	$1.8 \pm 1.5$	3.3				
<b>fine-particulate mass</b>									
FRM vs TEOM	44	0.97	$0.84 \pm 0.02$	0	1.1	18.8	2.9	2.2	12.4
		0.98	$0.94 \pm 0.02$	$-1.8 \pm 0.4$	0.9				
FRM vs PC-BOSS	41	0.89	$0.96 \pm 0.05$	0	2.3	18.9	0.7	1.6	8.5
nonvolatile mass		0.90	$0.88 \pm 0.05$	$1.5 \pm 0.9$	2.2				
FRM vs PC-BOSS	40	0.82	$1.16 \pm 0.02$	0	3.3	19.1	-3.1	NA <sup>c</sup>	
$PM_{2.5}$ mass		0.86	$0.96 \pm 0.06$	$3.8 \pm 1.3$	3.0				
PC-BOSS	42	0.89	$0.87 \pm 0.05$	0	2.2	17.4	2.2	NA <sup>c</sup>	
nonvolatile vs TEOM		0.90	$0.95 \pm 0.05$	$-1.3 \pm 0.9$	2.1				
D mass vs D CM <sup>d</sup>	29	0.31	$0.80 \pm 0.11$	0	1.1	2.3	-0.8	0.6	34
		0.54	$0.51 \pm 0.09$	$0.3 \pm 0.3$	0.9				

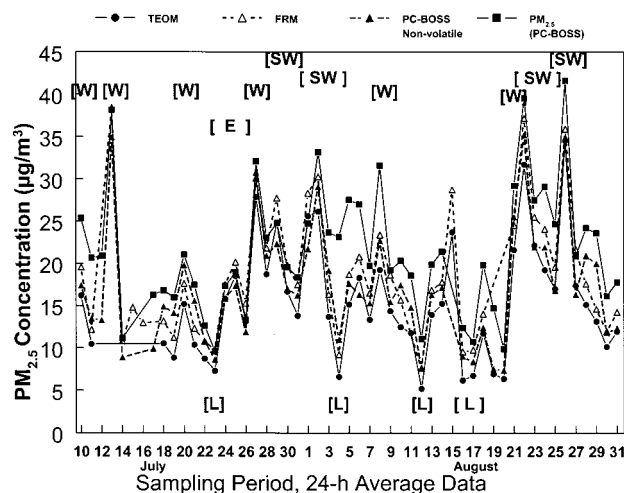
<sup>a</sup> Linear regression results are given for both a zero and calculated intercept. The uncertainties are the standard for the slope, intercept, and  $y$  estimate ( $Se_y$ ). <sup>b</sup> The precision  $\sigma$  is corrected for bias.<sup>9</sup> <sup>c</sup> The precision could not be calculated because the bias is too large. <sup>d</sup> D Mass vs D CM. The difference in mass for the PC-BOSS constructed nonvolatile mass vs the TEOM mass compared to the difference in PC-BOSS Quartz C vs R&P C Analyzer C.

**Figure 2.** Three-hour average TEOM measured fine-particulate mass concentrations for the period 10 July–31 August 2000.

the mass determined from the sum of the chemical constituents on the quartz and Teflon filters of the minor flow of the PC-BOSS sampler,  $Q_1$  and  $T_1$  in Figure 1. Total PC-BOSS  $PM_{2.5}$  mass was calculated as the sum of the nonvolatile mass and SVOC and ammonium nitrate lost from particles during sampling and trapped on the CIG and Nylasorb filters in the minor flow,  $C_1$  and  $N_1$  in Figure 1.

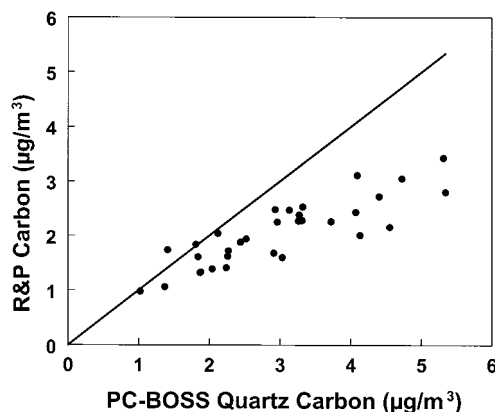
Concentrations of fine-particulate mass determined on a 3-h basis with the TEOM monitor are given in Figure 2 for the period from 10 July–31 August 2000. The TEOM monitor  $PM_{2.5}$  data are complete except for a period from 12 to 18 July. The TEOM monitor was down for maintenance during this time period. The day-to-day variation in fine-particulate mass concentrations illustrated in Figure 2 has been shown to be associated with changes in the transport of pollutants to the NETL site.<sup>4</sup>

Concentrations of fine-particulate mass determined on a 24-h basis with the TEOM monitor, with the  $PM_{2.5}$  FRM, and constructed from the nonvolatile filter con-

**Figure 3.** Comparison of 24-h average fine-particulate mass concentrations. The TEOM monitored was operated at 50 °C. The FRM mass is measured by the  $PM_{2.5}$  FRM sampler using EPA protocols (see text). PC-BOSS is the constructed non-volatile (filter retained) mass calculated from the PC-BOSS determined chemical components.  $PM_{2.5}$  is the total fine-particulate mass determined with the PC-BOSS including the semivolatile nitrate and organic material. Days when the meteorological source of the  $PM_{2.5}$  could be identified are also indicated. W is for transport to the NETL site from the west. SW is for transport to the NETL site from the southwest. E is for transport to the NETL site from the east to southeast. L is for locally generated pollutants. The size of the bracket is indicative of the length of the period considered for each meteorological transport condition. Exact days used are given in the text.

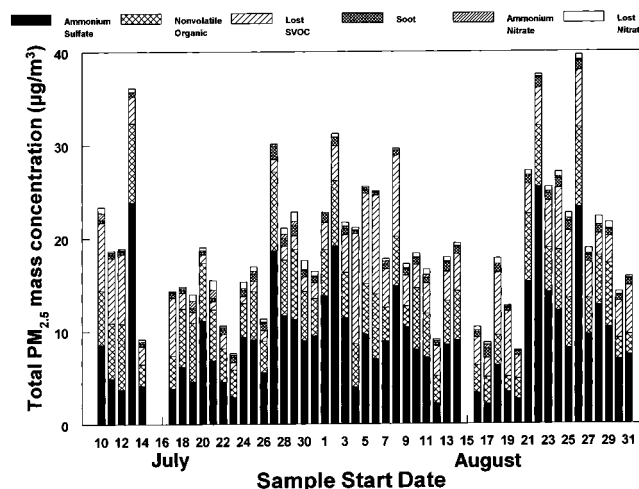
stituents determined with the PC-BOSS are compared in Figure 3. FRM and complete PC-BOSS data are available for 49 and 48 of the 53 days, respectively. There is general concurrence in the daily changes in fine-particulate mass seen with the three measurements. However, some consistent biases are seen among the three data sets, with the concentration generally increasing in the order  $TEOM < \text{nonvolatile PC-BOSS} < FRM < PM_{2.5}$  PC-BOSS mass. The regression and statistical analyses associated with these comparisons are given in Table 1.

(17) Turpin, B. J.; Lim, H.-J. Species Contributions to  $PM_{2.5}$  Mass Concentrations: Revisiting Common Assumptions for Estimating Organic Mass. *Aerosol Sci. Technol.* **2001**. In press.



**Figure 4.** Comparison of the total carbon retained on the quartz filters of the PC-BOSS and the R&P Carbon analyzer determined fine-particulate carbon collected on an impaction strip at 50 °C.

The observed differences can be attributed to the ways in which the three samplers handle the collection of semivolatile  $PM_{2.5}$  particulate material. The concentrations of ammonium nitrate were small and do not account for the variations in  $PM_{2.5}$  mass determined with the various samplers as shown in Figure 3. The concentrations of fine-particulate organic material were substantial. The PC-BOSS data indicate that, in addition to the filter retained nonvolatile organic material, a substantial fraction of the organic material consisted of semi-volatile compounds that can be lost from the particles collected on a filter. The Teflon coated particle collection filter of the TEOM monitor is heated to 50 °C to avoid the collection of water. Losses of semivolatile organic material with this filter are expected to be greater than for the other two samplers that collect particles at ambient temperature. This assumption can be further tested by comparison of the carbonaceous material collected on the quartz filter of the PC-BOSS and the carbonaceous material determined by the R&P carbon monitor, which collects particles on an impaction strip that is also heated to 50 °C prior to carbon analysis of the collected material. As indicated in Figure 4, the R&P determined carbon tended to be equal to or less than the PC-BOSS determined quartz filter carbon. The linear regression analyses of the difference between the R&P carbon monitor and PC-BOSS quartz filter determined carbon and the difference between the TEOM monitor determined mass and PC-BOSS constructed nonvolatile mass, Table 1, indicated that 60% of the mass difference between the two measurements could be accounted for by the observed differences in carbon measurements. The loss of organic material on the heated TEOM monitor filter may be somewhat larger than that for the heated R&P carbon analyzer impaction plate, since particles on the impaction plate also experience a lower pressure differential across their surface as compared to those on the TEOM filter. Thus, it is reasonable to assume that the differences in mass measurements for the TEOM monitor and the PC-BOSS nonvolatile mass are due to the increased loss of organic material by the heated TEOM filter. This loss of organic material from the heated TEOM filter accounts for an average difference in the mass measurement between the two methods of 9% of the PC-BOSS nonvolatile  $PM_{2.5}$  determined value.

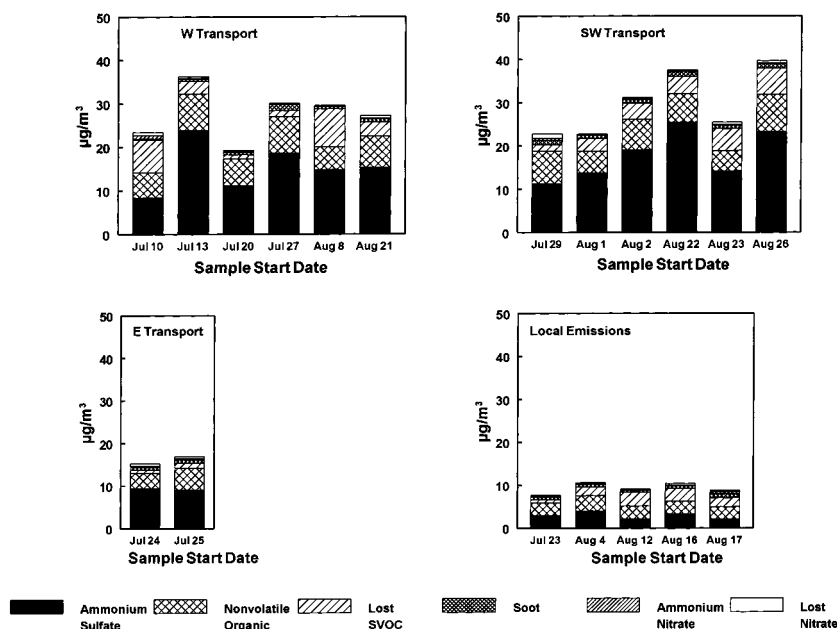


**Figure 5.** Daily  $PM_{2.5}$  chemical composition determined using the PC-BOSS. See text for details on each determined fine-particulate component. Fine-particulate crustal material is not included.

The average observed difference between the PC-BOSS nonvolatile mass and the FRM mass, Table 1, may also be attributed to the difference in collection and retention of semivolatile organic material on a filter by the two methods. With the PC-BOSS sampler, the particles are collected after a diffusion denuder designed to remove all gas-phase organic compounds. No denuder is present in the FRM sampling stream. Thus the difference between the mass determined by the FRM sampler and the lower (by an average of 5%) nonvolatile PC-BOSS mass may be due to the enhanced loss of SVOC from collected particles after the denuder of the PC-BOSS, as compared to that for the FRM sampler. However, since the FRM  $PM_{2.5}$  mass is lower than the PC-BOSS total  $PM_{2.5}$  mass (the nonvolatile mass plus the SVOC mass), the data also indicate that some SVOC material is also lost from the Teflon filter of the FRM sampler. When the lost semivolatile material is added to the nonvolatile PC-BOSS data to give a PC-BOSS total  $PM_{2.5}$  concentration, the resulting concentrations are higher than those observed using the FRM sampler, Table 1, with the apparent loss of SVOC from the Teflon filter of the FRM sampler averaging 16% of the total  $PM_{2.5}$  mass.

**$PM_{2.5}$  Composition.** Figure 5 illustrates the PC-BOSS determined daily variation in total  $PM_{2.5}$  mass. Also depicted are the compositional contributions from ammonium sulfate, nonvolatile ammonium nitrate, nonvolatile organic material, soot, and ammonium nitrate and SVOC lost from particles during sampling with the PC-BOSS. Soot concentrations were obtained from the R&P Carbon monitor results. The PC-BOSS carbon data were corrected for this amount of soot. The data have also been supplemented with FRM and RAAS results for three samples where the PC-BOSS results were incomplete. Combined lost and retained ammonium nitrate constituted an average of only 3.0% of the total  $PM_{2.5}$ , with an average of two-thirds of the ammonium nitrate being lost from the Teflon filter of the PC-BOSS during sampling. On average, 18% of the total  $PM_{2.5}$  was SVOC that was lost from collected particles during sampling. The SVOC concentrations ranged from 0.8 to 11.9  $\mu\text{g}/\text{m}^3$ . The presence of this level





**Figure 6.** Daily  $PM_{2.5}$  chemical composition determined using the PC-BOSS associated with specific transport paths. W is for transport to the NETL site from the west. SW is for transport to the NETL site from the southwest. E is for transport to the NETL site from the east to southeast. L is for locally generated pollutants.

of SVOC implies that single filter samplers will tend to significantly underestimate total  $PM_{2.5}$ . As outlined above, an average of about 2/3 of the SVOC lost from the quartz filter of the PC-BOSS was also lost from the Teflon filter of the FRM. Nonvolatile organic material (ranging from 1.6 to 8.6  $\mu g/m^3$ ) constituted an average of 23% of the total  $PM_{2.5}$  mass. Particulate ammonium sulfate concentrations (ranging from 2 to 25.4  $\mu g/m^3$ ) were the largest fraction of the fine-particulate material, averaging 43% of the  $PM_{2.5}$  mass.

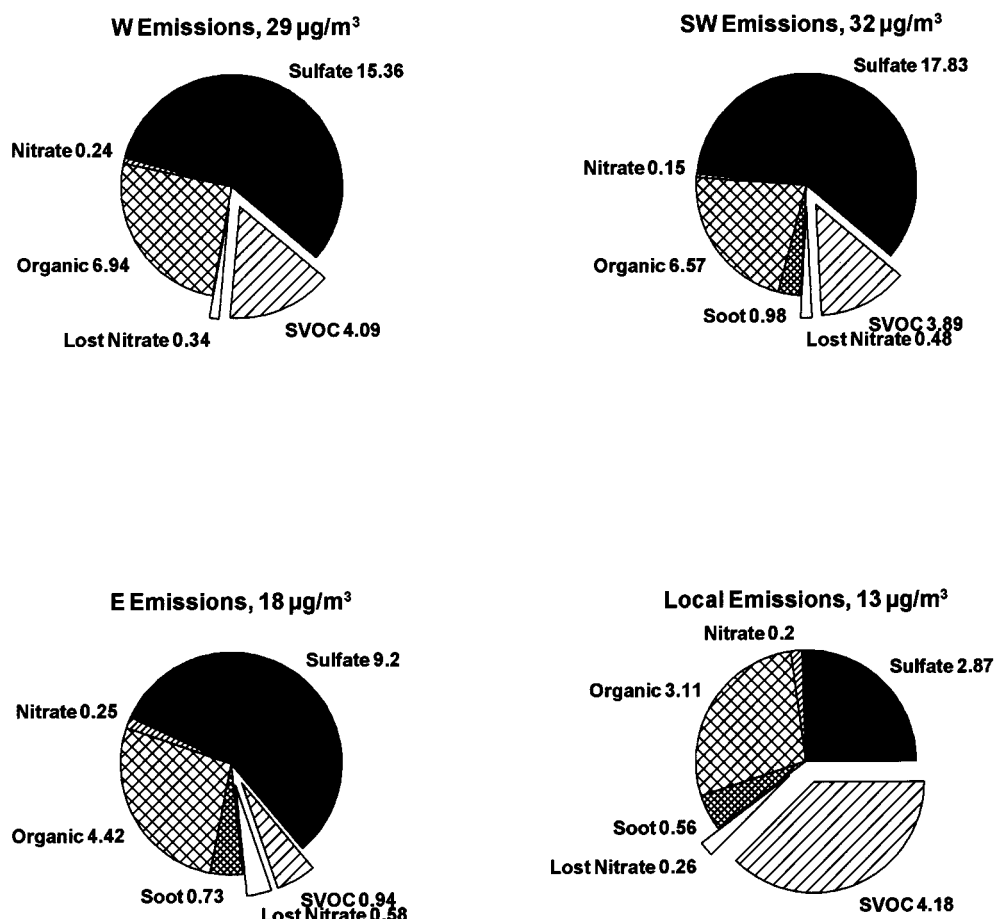
**Transport Specific  $PM_{2.5}$  Composition.** Surface weather maps<sup>18</sup> and estimated back-trajectories<sup>19</sup> have previously been used to determine the probable sources of pollutants present at the NETL sampling site for each study day.<sup>4</sup> These analyses indicated that during the time period included in this manuscript, pollutants present at the NETL site originated from four different source regions. High concentrations of  $PM_{2.5}$  were associated with the transport of pollutants from outside the immediate region of the site during the passage of a frontal system. The most common transport was from the Ohio River Valley to the southwest of the NETL sampling site (29 July and 1, 2, 22, 23, and 26 August, identified by SW in Figure 3). Pollutants from this region are expected to include significant emissions from the various coal-fired power plants in this region. Frequently pollutants were transported to the site directly from the west (10, 13, 20, and 27 July, and 8 and 21 August, identified by W in Figure 3). This transport path will include emissions from coal-fired power plants and various coke processing and steel manufacture facilities located along the Ohio River to the west of the NETL site. Transport on 8 August may have included emission from both the west and south-

west. July 24–25 was the only time period when significant concentrations of pollutants were transport to the NETL site from the east (identified by E in Figure 3). On these 2 days, transport was from the east to southeast. There was precipitation over eastern Pennsylvania during this period. The lowest concentrations of pollutants were associated with the presence of a high-pressure system over the sampling site, resulting in the buildup of locally emitted pollutants (23 July and 4, 12, 16, and 17 August, identified by L in Figure 3). During these time periods, the pollution present at the site will be dominated by transportation emissions and emissions from coal-fired boilers near the site.<sup>4</sup> The 24-h (or longer) time periods which were associated with transport from one of these four regions are indicated in Figure 3. Other days were transition periods when several source regions may have contributed to the airborne pollutants at the site. The chemical composition of the sampled  $PM_{2.5}$  for each day associated with one of these transport conditions is given in Figure 6, and the average chemical composition of particles present for each transport condition is given in Figure 7.

The lowest concentrations of  $PM_{2.5}$  were associated with local emissions. On these 5 days  $PM_{2.5}$  averaged 13.0  $\mu g/m^3$ , and ammonium sulfate concentration averaged only 2.9  $\mu g/m^3$ , 22% of the total. SVOC was the largest fraction of the fine-particulate material and the carbonaceous material totaled 70% of the identified  $PM_{2.5}$ . This is consistent with the expected high influence of local transportation sources. Concentrations of  $SO_2$  for these samples averaged 4.8 ppm, lower than the concentrations associated with samples from the SW (7.7 ppm) or W (8.7 ppm), but higher than concentrations associated with transport from the east (3.1 ppm). This suggests there was impact from local coal-fired boilers. However, the fractional conversion of  $SO_2$  to sulfate was low for these samples. Concentrations of  $NO_2$  and  $NO_x$  averaged 10 and 13 ppb, respectively. These were among the highest concentrations seen for

(18) UNISYS 2001 <http://www.weather.unisys.com/surface/index.html>.

(19) HYSPLIT4 (HYbrid Single-Particle Lagrangian Integrated Trajectory) model, 1997. Web address: <http://www.arl.noaa.gov/ready/hysplit4.html>, NOAA Air Resources Laboratory, Silver Spring, MD. (NETL is located at 40.307, -79.979.)



**Figure 7.** Average PM<sub>2.5</sub> chemical composition ( $\mu\text{g}/\text{m}^3$ ) determined using the PC-BOSS associated with specific transport paths. W is for transport to the NETL site from the west. SW is for transport to the NETL site from the southwest. E for for transport to the NETL site from the east to southeast. L is for locally generated pollutants.

this time period, again indicating the significant impact of local transportation emissions.

PM<sub>2.5</sub> mass associated with emissions from the east, Figures 6 and 7, averaged about 50% higher than emissions from the local region,  $18 \mu\text{g}/\text{m}^3$ . However, ammonium sulfate associated with this PM<sub>2.5</sub> was 3 times higher than that in PM<sub>2.5</sub> of local origin, averaging  $9.2 \mu\text{g}/\text{m}^3$ . The concentration of SO<sub>2</sub> in these transported emissions was lower than seen in local emitted material, averaging 3.1 ppm. Thus, the fraction of SO<sub>2</sub> converted to sulfate was much higher for emissions transported into the region from the east. The concentrations of NO<sub>2</sub> and NO<sub>x</sub> were comparable to those when local emissions dominated, averaging 11 and 16 ppm, respectively. The concentrations of SVOC in these samples was low and ammonium sulfate accounted for 52% of the fine-particulate mass. The composition of emissions from the east are consistent with emissions similar in composition to those produced locally, but more aged, resulting in more conversion of SO<sub>2</sub> to ammonium sulfate and loss of SVOC.

Emissions from both the west and southwest are associated with much higher concentrations of SO<sub>2</sub> and sulfate. The composition of fine-particulate material transported to the NETL site from these two directions were comparable, Figure 7. Ammonium sulfate and SO<sub>2</sub> averaged  $15.4 \mu\text{g}/\text{m}^3$  and 8.7 ppb from the west and  $17.8 \mu\text{g}/\text{m}^3$  and 7.7 ppb from the southwest. Ammonium

sulfate averaged 53% and 55% of the PM<sub>2.5</sub> mass from the west and southwest, respectively. Concentrations of carbonaceous material and the fraction of organic material present as SVOC were comparable for PM<sub>2.5</sub> transported to the NETL site from these two source regions. More nitrogen oxides were associated with emissions transported to the NETL site from the southwest than from the west. The concentrations of NO<sub>2</sub> and NO<sub>x</sub> from the southwest averaged 9.1 and 10.6 ppm, respectively. The concentrations of NO<sub>2</sub> and NO<sub>x</sub> from the west averaged 6.8 and 7.3 ppm, respectively. The high concentrations of sulfate and SO<sub>2</sub> in the air masses transported from the west and southwest suggest that emissions from coal-fired boilers significantly influence the pollutants transported from both of these directions, since these facilities are the major SO<sub>2</sub> sources in the region.

**SAS and Elemental Markers in Transported Air Masses.** The suggested sources for emissions that are transported to the NETL site from the south and southwest can be checked using the available SEM<sup>12</sup> and PIXE analyses results. PIXE data are available for most of the transport specific (Figure 3) samples. The concentration of iron in PM<sub>2.5</sub> transported to the NETL site from the west varied from 0.003 to  $0.050 \mu\text{g Fe}/\text{m}^3$  and averaged  $0.030 \mu\text{g Fe}/\text{m}^3$ . August 20 was the only day for this sample set the Fe concentration was below  $0.02 \mu\text{g Fe}/\text{m}^3$ . Concentrations of fine-particulate Ca



correlated with the concentrations of Fe and averaged  $0.026 \mu\text{g Ca/m}^3$ . Both elements are expected in emissions from iron processing facilities along the Ohio River to the west of the NETL site. These trace element concentrations are consistent with the back-trajectory estimate source origins. In contrast, concentrations of Fe and Ca associated with transport from the southwest averaged  $0.001 \mu\text{g Fe/m}^3$  and  $0.006 \mu\text{g Ca/m}^3$ , and had maximum concentrations of  $0.003 \mu\text{g Fe/m}^3$  and  $0.011 \mu\text{g Ca/m}^3$ . This is consistent with the expected lack of emission from iron processing industries from this source region. Thus, Fe and Ca data may allow discrimination between emission from coal-fired boilers located to the southwest and from coke and iron processing industries to the west of the NETL site.

SEM data are available for even days from 6–18 August. As indicated in Figure 3, transport was expected to be dominantly from the west on 8 August, and local emissions were expected to dominate on 12 and 16 August. August 6 was a transition day with transport from both the southwest and west. The highest concentrations ( $0.87 \mu\text{g/m}^3$ ) of SAS particles from coal-fired power plants were observed on this day with low, SEM measured, concentrations of Fe rich spherical particles ( $0.06 \mu\text{g/m}^3$ ), but moderate, PIXE determined, concentrations of Fe ( $0.07 \mu\text{g Fe/m}^3$ ), Ca ( $0.03 \mu\text{g Ca/m}^3$ ), and SEM measured Ca/S rich particles ( $0.30 \mu\text{g/m}^3$ ). Both the SEM and PIXE results are consistent with emissions from both the west and southwest at the NETL site this day. The next sample day, August 8, when transport was dominantly from the west, SAS concentrations dropped to  $0.24 \mu\text{g/m}^3$ . The concentration of Ca/S rich particles ( $0.51 \mu\text{g/m}^3$ ) was still elevated, but Fe rich spherical particles were not detected. Corresponding PIXE data are not available for this day. These observations are consistent with a high contribution of  $PM_{2.5}$  from coal-fired boilers on 6 August, but the expected contribution from iron processing industries on 8 August was only partially confirmed with the SEM data for the Ca/S rich particles.

On 12 and 16 August, local emission are predicted to dominate. On these 2 days, concentrations of Fe rich spherical particles were  $0.09 \mu\text{g/m}^3$  and not detectable, respectively. Ca/S rich particle concentrations were low on 12 August ( $0.07 \mu\text{g/m}^3$ ) but high on August 16 ( $0.67 \mu\text{g/m}^3$ ). SAS particle concentrations were  $0.09 \mu\text{g/m}^3$  and  $0.26 \mu\text{g/m}^3$ , respectively. These concentrations are consistent with minimal transport of emissions from the west with some influence of emissions from local coal-fired power plants, as predicted by the meteorological analyses above. August 10 and 18 were both days when there was precipitation in the region, with low pressure and transport of air masses from the north on 10 August and establishment of a high after the precipitation on 18 August. Total  $PM_{2.5}$  mass and concentrations of various  $PM_{2.5}$  components were almost identical both days. Total  $PM_{2.5}$  mass averaged  $20.8 \mu\text{g/m}^3$ , with relatively high concentrations of ammonium sulfate ( $8.0 \mu\text{g/m}^3$ , 38% of the total  $PM_{2.5}$  mass), but low concentrations of SAS particles ( $0.05 \mu\text{g/m}^3$ ) and Fe rich spherical particles ( $0.16 \mu\text{g/m}^3$ ). Ca/S rich particles were not detected on August 10 but elevated on August 18 ( $0.4 \mu\text{g/m}^3$ ). Concentrations of  $\text{SO}_2$  were low (4 ppb). These results suggest that the site was dominated by trans-

portation and urban source emissions but with higher conversion of  $\text{SO}_2$  to sulfate, presumably associated with the presence of clouds. These results are comparable to those seen on 24 and 25 July with transport from the east and precipitation to the east. On 14 August, the high-pressure system present on August 12 and 16 still influenced the NETL site, with some transport from the north. The higher concentrations present at the NETL site on 14 August ( $21 \mu\text{g/m}^3$ ) compared to that on 12 and 16 August ( $\sim 12 \mu\text{g/m}^3$ ), may represent an impact from the west. Concentrations of SAS particles ( $0.08 \mu\text{g/m}^3$ ) are not consistent with transport from the southwest, but the concentration of Fe rich spherical particles ( $0.22 \mu\text{g/m}^3$ ) suggests some influence from iron processing industries, that exist along the Ohio River both to the west and northwest of the NETL site.

Examination of the use of PIXE and SEM data as tracers of emission sources impacting the NETL site is continuing. Markers of emissions from iron and coke processing industries, and the extent to which Fe may be emitted by both coal-fired boilers and iron processing industries, need to be better established.

### Conclusions

The mass and composition of  $PM_{2.5}$  present at the NETL Pittsburgh sampling site are dependent on meteorological transport. During high-pressure conditions, concentrations of  $PM_{2.5}$  are the lowest and the composition is dominated by carbonaceous material. Under these meteorological conditions, the fine-particulate matter originates mainly from local transportation emissions and some coal-fired boiler emissions. Conversion of  $\text{SO}_2$  to sulfate was nominal. High concentrations of  $PM_{2.5}$  were always associated with transport of pollutants to the NETL site with the passage of a frontal system after a period of high pressure. This results suggests that these high  $PM_{2.5}$  concentrations originate from larger, more distant emission sources. Back-trajectory analysis suggests these pollutants originate from emission sources along the Ohio River Valley to the west or southwest. The main component of  $PM_{2.5}$  associated with this transport is ammonium sulfate. Limited SEM and PIXE results suggest that when transport is from the west, the emissions originate from both coal-fired boilers and the coke and steel processing facilities along the Ohio River to the west of the NETL site. The expected markers for emissions from the iron industries are not present when the pollutants are transported to the NETL site from the southwest. Under these conditions, coal combustion along the Ohio River Valley to the southwest may be an important contributor to the  $PM_{2.5}$  mass seen at the NETL site.

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